

PATENT SPECIFICATION

1,082,725

1,082,725



Inventors: DAVID ALEXANDER WOLTON, DAVID ATTWOOD
and JAMES EDWARD FREDERICK MARSHALL.

*Date of filing Complete Specification (under Section 3 (3) of
the Patents Act 1949):* June 9, 1964.

Application Date: June 13, 1963.

No. 23659/63

Application Date: October 29, 1963.

No. 23642/64

Complete Specification Published: September 13, 1967.

© Crown Copyright 1967.

Index at Acceptance:—C6 EH; A2 B6A.

Int. Cl.:—C 12 c 3/00, C 12 c 9/02 // A231.

COMPLETE SPECIFICATION

NO DRAWINGS

Method of obtaining Flavouring Ingredients from Hops

We, WOLTON HOP EXTRACTS LIMITED, a British Company, of 27 Borough High Street, London, S.E.1., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of obtaining flavouring ingredients from hops, and to the flavouring ingredients obtained thereby.

According to the invention, flavouring ingredients are obtained by subjecting hops, preferably after they have been dried, or a hop resin-containing fraction derived from hops, to solvent extraction using an organic solvent which is substantially immiscible with water, partitioning the organic extract with an aqueous alkaline solution, and separating the aqueous phase from the organic phase. It has been found that by this means there can be obtained an alkaline solution of hop resins which, after neutralisation, provides a useful flavouring agent, particularly but not exclusively for beer. Further flavouring material, in the form of hop oils, can be recovered from the organic phase by distilling off the solvent and then steam distilling the residue.

The starting material will frequently be whole dried hops or hops waste, e.g. waste material from the picking machine, (both of which are included within the term "hops" wherever the context permits); but it may also be a fraction derived from hops or hop waste, in particular the lupulin-rich product obtained by the process described in our British Specification No. 42689/63 (Serial No. 1082726); this process comprises mechanically disintegrating the hops or hop material and then screening, preferably on a 50 mesh screen (openings

about 0.3 mm) and especially an 80 mesh screen (openings about 0.18 mm.), to remove the coarser particles, the finer particles then constituting the lupulin-rich material. An advantage of using this material is that it has a higher resin content than whole hops or hop waste, and also is free from seeds.

The solvent extraction of the hops may be carried out in any suitable way, for example by macerating them in contact with or stirring them with, the organic solvent. Stirring without maceration is often preferable, as maceration tends to break down the hop petal cell structure and releases seed fats which for some purposes are undesirable.

The organic solvent for the extraction will normally be a normally liquid hydrocarbon. For example, aliphatic hydrocarbons such as pentane and its higher homologues and mixtures thereof, petroleum spirit fractions with boiling points in the ranges 40°-60°C., 60°-80°C., and 80°-100°C., and also aromatic hydrocarbons such as benzene homologues, e.g. toluene, may be used. Chlorinated hydrocarbons such as methylene chloride can also be used, but their physiological properties will generally make them less advantageous, as also is the case with benzene. On the other hand, highly halogenated hydrocarbon solvents, e.g. carbon tetrachloride, chloroform, trichloroethylene, tetrachloroethylene, and hexachloroethane have the very important practical advantage of relatively low flammability, and may often be used on this account: the unsaturated compounds are preferred as they are more stable towards alkali. Ethers, e.g. diethyl, diisopropyl and dibutyl ethers, are also of use, being useful especially when the isolation of hop oils is important. A solvent of relatively low boil-

[Price

ing point is preferred, especially when it is desired to obtain hop oils and ease of distillation is advantageous.

Preferably the solvent is employed in amount and under conditions such that the humulone content of the extract does not exceed 8%, and is advantageously in the neighbourhood of 4%, say 3-5%.

For most purposes it is preferred to filter the extract before subjecting it to partition with the aqueous alkaline solution.

The partition with an alkaline solution may be carried out simply by mixing the alkaline solution with the extract at atmospheric temperature, vigorously agitating the mixture and allowing the two liquid phases to settle. However, when carrying out the partition on a continuous basis, which is normally desirable a countercurrent partition method may be used. Countercurrent methods use, for example, a vertical column containing plates or a solid packing or baffles or the like, one liquid being caused to travel up the column and the other down the column, and are in themselves well known.

Suitable alkaline solutions for the partition include solutions of alkali metal hydroxides and solutions of alkali metal carbonates and bicarbonates and alkaline earth metal hydroxides. Caustic soda solution is preferred and may be used in concentrations down to 0.5% or even lower, and up to 7% or higher. A suitable range is 0.5-5%, and especially 0.5-3%. The carbonates and bicarbonates can be used in similar or higher concentrations, preferably however with a minimum of about 2%. (All concentrations are on a weight/volume basis). Whatever the alkali used, the concentration employed will in practice usually be near the lower end of the useful range, if only for reasons of economy. The organic phase remaining after the alkali treatment can be recycled to the extraction step; after it has been used several times, e.g. 5 times or more, hop oils can be recovered from it as described below.

The alkaline extract containing the hop resins may be used after acidification, preferably to pH 2-4, e.g. with hydrochloric acid in any convenient concentration, especially 1-12% for such purposes as incorporation in beer to give the characteristic aroma and taste. Alternatively, after the acidification the resins, which now form a separate phase, can be allowed to settle and then be separated, or removed in some other way as by centrifuging, if desired being further worked up, e.g. by washing with water to remove salts and drying in the absence of oxygen, before their use as flavouring ingredients. Preferably at some stage before the resins are dried a protective colloid is added to them to prevent

agglomeration; examples of suitable additives are methyl cellulose, alginates and alginic acid, and the materials known as "finings" and commonly used in clarifying beer. Naturally the protective colloid should be physiologically innocuous. Especially when no protective colloid is present the acidification may be carried out in the presence of a carrier, such as a diatomaceous earth or silica gel, preferably in amount between about 5 and 200%, especially 20 to 100%, of the weight of the hop resins, on which the resins are found to precipitate. Naturally the carrier should be physiologically innocuous and insoluble in the solutions concerned.

The hop resins may, if desired, be given before use a treatment whereby the humulone and other constituents of the α -acids (cohumulone and adhumulone) are isomerised, i.e. are converted into the corresponding iso-compounds. This can be done by heating the alkaline solution of the resin, or otherwise heating the resin with alkali, in the absence of oxygen to a temperature above 70°C., preferably 80-130°C., under pressure if necessary, for a time which will naturally depend on the temperature; usually 45 minutes will suffice at 100°C., and 15 minutes at 120°C. When, as is preferred, the resin is isomerised in the alkaline solution obtained from the partition, the alkali solution obtained from the partition should initially be de-oxygenated (as also should any separate alkali solution used). The concentration of the alkali employed for the isomerisation should not exceed 0.5% in the case of a caustic alkali, or 3% in the case of an alkali metal carbonate, so as to avoid degradation to humulic acid. Suitable concentration ranges in the two cases are 0.25-0.4% and 1-3%, respectively. Thus if a more concentrated alkali has been used for the partition it may be diluted or partially neutralised before the isomerisation; alternatively a caustic alkali may be converted into the corresponding carbonate as by passing carbon dioxide through the solution. The solution resulting from the isomerisation may be acidified, e.g. to pH 2-4, and then, if desired, extracted with an organic solvent, e.g. a hydrocarbon or other solvent such, for example, as a light petroleum fraction or other mixture of light aliphatic hydrocarbons. A description of an isomerisation process is contained in British Specification No. 855,401.

As stated above, hop oils can be obtained from the organic residue resulting from the partition, preferably after the solvent has been recycled to the extraction step several times. To this end the solvent may be removed by simple distillation, if desired

under reduced pressure, after which the oils can be obtained by steam distillation of the residue. Usually about 3 ml. of oils will be obtained from 1 kg. of hops, using say 40 litres of solvent and recycling it several times. The hop oils may also be incorporated in beer or used for other flavouring purposes.

In another method the used solvent may be dried, as by filtration or by passing it over a dessicant, and then passed through a column of dry silica gel which will absorb the so-called oxygenated fraction of the oils.

It is an advantage of the invention that the hops are not treated directly with alkali, and that the alkali that is used need be in low concentrations only and at normal temperatures.

The following Examples illustrate the invention, parts being by weight.

EXAMPLE I

20 parts of hops are stirred with 320 parts of petroleum spirit, 60°-80°C. fraction, for 5-10 minutes and the mixture filtered. 50 parts of 5% caustic soda solution are added to the filtrate and the mixture vigorously agitated for 2 minutes and allowed to separate for 10 minutes. The alkali is run off and 2 parts of a diatomaceous earth ("Johns Manville Standard Supercel") is added. The solution is acidified to pH 2-3 with 10% hydrochloric acid while stirring, causing the resins to precipitate on the carrier. The precipitate is allowed to settle or is separated by centrifuging, after which it is washed with water and dried to a powder, which is very suitable for use as a flavouring agent, e.g. in the manufacture of beer. Alternatively, the neutralised solution is itself used directly as a flavouring agent, the carrier and the resins being kept in suspension by stirring if necessary.

A similar product is obtained when the partition is effected continuously by passing the filtered organic solvent extract up a packed column and causing the caustic soda solution to flow down the column, the alkaline extract being run off at the bottom of the column.

EXAMPLE II

The process of Example I is repeated, using as the solvent

- (a) the same petroleum spirit fraction
 - (b) trichloroethylene
 - (c) toluene
 - (d) dibutyl ether
- and as the alkaline solution a 2.5% caustic soda solution. Similar results were obtained.

In the run in which dibutyl ether was used as the solvent, the organic residue from the partition was used repeatedly until 500 g. of hops had been treated. The dibutyl ether was then distilled off, and the residue steam distilled. About 1.5 cc. of hop

oils separated from the distillate.

EXAMPLE III

An alkaline solution of hop resins obtained as in Example II, using trichloroethylene as the organic extractant, and a de-oxygenated caustic soda solution, is diluted to a caustic soda concentration of 0.3% and then boiled under atmospheric pressure for 45 minutes. It is then acidified quickly to pH 3 with hydrochloric acid, and about 0.2% methyl cellulose is added. The resulting precipitate is allowed to settle, is washed with water, adjusted to pH 6.5-7.5, the same amount of methyl cellulose is added again, and the precipitate is dried to a powder in the absence of oxygen by either a vacuum or a freeze drying method.

EXAMPLE IV

20 parts of lupulin are stirred with 150 parts of trichloroethylene for 5-10 minutes, 85 the mixture obtained is filtered, and the filter cake washed on the filter with 30 parts of trichloroethylene. The filtrate and washings are combined, and extracted by partitioning and separating three successive times with 40 parts of a 3% (weight-volume) de-aerated aqueous solution of sodium carbonate.

The three aqueous extracts so obtained are mixed together, and the resulting solution is heated to 100°C. for 45 minutes; it is then cooled and acidified quickly to about pH 3 with hydrochloric acid, with the addition of the same diatomaceous earth as in Example I. The precipitate is allowed to settle, and after being freed from the supernatant liquid is washed with water and adjusted to pH 6.5-7.5. It is then dried to a powder in the absence of oxygen.

If desired the addition of the diatomaceous earth can be omitted and the precipitated resins allowed to settle by themselves or centrifuged out of the solution.

This Example can also be carried but by performing the partition continuously in a column, the trichloroethylene extract flowing downwards against an upward flowing stream of the alkaline solution. By both methods a good yield of the dried flavouring material is obtained.

The trichloroethylene can be replaced by benzene, toluene or perchloroethylene without substantially affecting the results obtained.

WHAT WE CLAIM IS:—

1. A process for the production of flavouring ingredients, which comprises subjecting hops to solvent extraction using an organic solvent which is substantially immiscible with water, partitioning the organic extract with an aqueous alkaline solution and separating the aqueous phase from the organic phase.

2. A process for the production of flavouring ingredients, which comprises sub-

- jecting a hop-resin containing fraction derived from hops to solvent extraction using an organic solvent which is substantially immiscible with water, partitioning the organic extract with an aqueous alkaline solution and separating the aqueous phase from the organic phase.
3. Process according to claim 1 or 2, wherein the hops or hops fraction are extracted with a normally liquid hydrocarbon solvent.
4. Process according to claim 1 or 2, wherein the hops or hops fraction are extracted with pentane or a higher homologue of pentane or a mixture of such hydrocarbons, petroleum spirit of boiling point between 40° and 100°C., or a normally liquid homologue of benzene.
5. Process according to claim 1 or 2, wherein the hops or hops fraction are extracted with one or more unsaturated highly halogenated hydrocarbon solvents.
6. Process according to claim 1 or 2, wherein the hops or hops fraction are extracted with a dialkyl ether.
7. Process according to any one of the preceding claims, wherein the organic extract is partitioned with an aqueous solution of an alkali metal or alkaline earth metal hydroxide.
8. Process according to any one of claims 1 to 6, wherein the organic extract is partitioned with an aqueous solution of an alkali metal carbonate or bicarbonate.
9. Process according to any one of the preceding claims, wherein the separated aqueous phase is acidified.
10. Process according to claim 9, wherein a finely divided carrier is added to the aqueous phase before, during or after the acidification.
11. Process according to any one of the preceding claims, wherein the organic fraction remaining after the separation of the aqueous phase is employed for the treatment of further hop material, and after it has been so used a number of times is treated to recover hop oils therefrom.
12. Process according to claim 11, wherein the organic solvent is distilled off from the extracted material which it still contains after the partition, the residue is steam distilled, and hop oils are isolated from the distillate.
13. Process according to any one of 55 claims 2-12, wherein a lupulin-rich material is extracted, said material having been obtained by mechanically disintegrating hops or hop waste and removing the coarser particles, the finer particles then constituting the lupulin-rich material.
14. Process according to claim 13, wherein the coarser particles are removed by screening through openings at most 0.3 mm. across.
15. Process according to any one of the preceding claims, wherein the hop resins obtained are subsequently given a treatment with a hot alkaline solution whereby humulones are isomerised to isohumulones.
16. Process for the production of flavouring ingredients substantially as described in the foregoing specific Examples.
17. Flavouring ingredients obtained by a process claimed in any one of claims 1 to 16.
18. Flavouring ingredients according to claim 17 in the form of a powder comprising hop resins deposited on a finely divided physiologically innocuous carrier or associated with a physiologically innocuous protective colloid.
19. Flavouring ingredients according to claim 17 in the form of a powder comprising isomerised hop resins deposited on a finely divided physiologically innocuous carrier or associated with a physiologically innocuous protective colloid.
- J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square,
Gray's Inn,
London, W.C.1.